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Blue Pigments in XVI-XVII Century Glazes: A Comparative Study between Portuguese Faiences and Chinese Porcelains

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Abstract. The trade of Chinese blue-and-white porcelains to Europe became intense along the XVII century following the maritime contact first established by the Portuguese navigators by the end of XVI century and nowadays European museums and traders face an increased need for ascertaining the authenticity of such art objects through non-destructive tests. With this purpose, a research project is being carried out on glazed faience and porcelain fragments collected during recent archaeological excavations by applying both laboratory techniques - X-ray fluorescence spectrometry and X-ray diffraction, instrumental neutron activation analysis - and X-ray absorption spectroscopy using synchrotron radiation at the European Synchrotron Radiation Facility in Grenoble/France. The blue chromophore role of cobalt in the glazes is discussed in relation to the speciation state and coordination environment of this element within the glassy silica-rich matrix. The results of both near-edge and extended fine structure analysis of Co 1*s* XAFS spectra are described and discussed, confirming the expected valence state (2+) of cobalt ions hosted as glass-forming components with an average coordination number close to four and a mean Co-O distance of about 2.0 Á. A confirmation of preliminary dating by Art Historians based on stylistic features is attained, taking into account the bulk chemistry of the glazes, particularly the presence or absence of lead and arsenic plus the relative contents of manganese, and iron versus cobalt.

Keywords: Blue glazes; cobalt speciation; ancient Chinese porcelains; contemporary Portuguese faiences.

INTRODUCTION

Ancient blue glazes owe their color mainly to copper and cobalt, either employed separately or added together to the siliceous matrix to attain the desired tonality. Once the speciation sates assumed by these two chromophore elements control the final coloring effect, X-ray absorption using synchrotron radiation (XAFS) is a particularly suitable spectroscopic technique for interpreting the pigment performance. The analysis of both near-edge features (XANES) and extended fine structure (EXAFS) of X-ray absorption spectra has been successfully used to study not only chromophore ions but also modifier elements in other ancient glassy materials, namely tile glazes [e.g., 1-4].

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established by the Portuguese navigators by the end of XVI century. European museums and traders have nowadays an increased need to ascertain the authenticity of such art objects through non-destructive assays. As a contribution to this subject, a XAFS study was carried out to characterize cobalt speciation plus coordination environment and tentatively confirm the Art-Historians' dating of a set of Chinese porcelain fragments supposedly manufactured in the XVI cent. A.D. (late Ming period, 1368-1644) and of glazed faiences with Chinese-type decorations recovered during recent archaeological excavations (Figure 1) conducted at the Monastery of Santa Clara-a-Velha in Coimbra, central Portugal [5], and in Lisbon Old-City.

The results of this study are described and discussed in conjunction with bulk chemical data obtained by a non-invasive X-ray fluorescence spectrometry qualitative assay.

FIGURE 1. Studied fragments of Chinese blue-and-white porcelains and contemporary Portuguese faiences.

PROBLEMATIC

With the aim of accurately dating the ceramics, thermo-luminescence (TL) tests were conducted over the faience fragments of Portuguese production collected at the already mentioned archaeological sites [6]. Regrettably, the reduced thickness of Chinese porcelain shards hindered the performance of TL tests. The problematic related to the studied archaeological shards is accordingly summarized in Table 1.

Ancient Chinese porcelains have been lately the object of many compositional studies applying X-ray and proton beam analytical techniques (namely, PIXE) to ascertain production periods and sites [e.g., 7-9]. It is known [10] that a shift from imported arsenic-rich Persian cobalt-based pigments towards native Chinese blue pigmenting ores - asbolane, a cobalt-containing manganese wad - has occurred during the early Ming Dynasty. This fact has rendered possible to outline a dating criterion based on the presence or absence of arsenic plus a combination of Mn/Co & Fe/Co ratios in the glaze.

The blue pigmenting properties of cobalt (2+) ions in tetrahedral coordination were established already forty years ago for Thenard's blue (ideally $CoAl_2O_4$, a spinel-type phase), and were recently reappraised for various cobalt pigments [11]. Beyond ascertaining the bulk chemistry of ancient blue glazes, another relevant purpose of the present work was then to confirm and validate the cause of coloring by studying cobalt speciation state in the glazes.

EXPERIMENTAL

The non-destructive chemical study was performed using a Philips PW1400 wavelength-dispersive X-ray fluorescence spectrometer (XRF-WDS) equipped witha rhodium tube and a LiF200 analyzing crystal. A verysmall fragment taken from the larger pieces or the whole fragment in the case of smaller samples (nrs. 94, 95, 428, Figure 1) were irradiated and fixed-time counting was carried out over the K_α diagnostic peaks of the relevant transition metals - Mn, Fe, Co, Cu. In view of the superposition of Pb L_α line and As K_α, the K_β peak of arsenic and the L_γ peak of lead were also measured to ascertain the presence of these elements.

TABLE 1. Dating problematic of studied archaeological shards.

Sample	Site and date of excavation	Dating problematic
94 and 95, Chinese porcelain fragments	*Monastery of Santa Clara-a-Velha* in Coimbra, central Portugal (<2003)	Very thin shards not suitable for thermo-luminescence dating
425, *id.*	*Rua da Madalena* in Lisbon (2007)	Chinese "Wanli" piece; 1573-1619 ?
426 and 428, *id.*	*Calçada do Lavra* in Lisbon (2004-5)	Also Chinese; 16th century; 2nd half ?
442, faience of Portuguese manufacture	*Id.* (2007)	17th cent., 1st half ? Identical to faience pieces were found in Hamburg, Germany
442, Portuguese faience		*Id.*; imitation of "Kraack" porcelain

TABLE 2. Chemical data obtained by X-ray fluorescence spectrometry in wavelength dispersion mode.

Sample reference	**94**	**95**	**425**	**426**	**428**	**442**	**446**
Element (20º)	Counts–per–second at the angular position						
Background (71.00)	360	314	123	112	190	182	188
Mn K_α (62.97)	**14 376**	**22 229**	**8 557**	**4 524**	**47 638**	409	378
Fe K_α (57.52)	**102 270**	**104 162**	**9 836**	**27 001**	**67 388**	6 501	17 024
Co K_α (52.80)	**5 522**	**3 649**	**1 841**	**1 414**	**11 073**	2 016	13 868
Mn / Co *ratio*	***2.6***	***6.1***	***4.6***	***3.2***	***4.3***	*0.2*	*< 0.1*
Fe / Co *ratio*	***18.5***	***28.5***	***5.3***	***19.1***	***6.1***	*3.2*	*1.2*
Cu K_α (45.03)	2 969	2 523	361	1 704	2 045	18 551	759
Co / Cu *ratio*	*1.8*	*1.8*	*5.0*	*0.8*	*5.0*	*0.1*	*18.3*
As K_α+ Pb L_α (34.00)	2 163	2 188	296	959	1 531	**40 813**	**91 633**
As K_β (30.45)	2 063	1 875	275	948	1 144	490	1 437
Pb L_γ (24.07)	2 359	2 112	273	1 025	1 208	**3 388**	**6 655**
Background (21.50)	2 535	2 242	277	1 010	1 252	297	225

Spectra background was measured at the limits of the angular 2θ region of interest (21.50º and 71.00º); the registered counts (Table 2) roughly reflect the comparative size of irradiated samples.

Co 1*s* X-ray absorption spectra were collected using the instrumental set-up of beam line BM-29 at the European Synchrotron Radiation Facility (ESRF in Grenoble/France) by directly irradiating the glazed debris and detecting the fluorescence yield using a germanium detector. The energy was calibrated with a cobalt metal foil. Along with well crystallized cobalt silicate ($Co_2 Si O_4$), a commercial blue pigment based on $Co Al_2 O_4$ (which phase constitution was checked by X-ray diffraction) were both irradiated to model cobalt speciation and coordination environment in the glazes.

RESULTS AND DISCUSSION

Chemical results obtained through the XRF-WDS non-invasive assay (Table 2) rule out the presence of arsenic in the glazes of porcelain shards; indeed, the count-rate values at Pb L_γ, As K_β and the energy-coincident L_α and K_α emission lines respectively from Pb and As are too close to for each porcelain sample; conversely, corresponding values for the two faience samples confirm the presence of significant contents of lead in the glaze, as expectable for a Portuguese XVII century manufacture.

Clearly distinct Mn/Co and Fe/Co ratios were obtained for thin (94-95-426) and thick (425-428) porcelain fragments, indicating that the first have a significantly higher iron content compared to manganese. Considering analytical results obtained for Ming porcelains by synchrotron X-ray fluorescence (SR-XRF) [9] and PIXE [8, 10], obtained ratios agree with the advanced dating (late XVI to early XVII century, Table 1).

The Co *K*-edge X-ray absorption (XAFS) spectrum of the glaze (Figure 2) display the same general trend for all fragments: a relatively intense pre-edge feature centered at ~7709 eV, the edge at an energy (7718 eV) indicative of a divalent state of the cobalt ions and a subsequent poorly detailed EXAFS region (Figure 3).

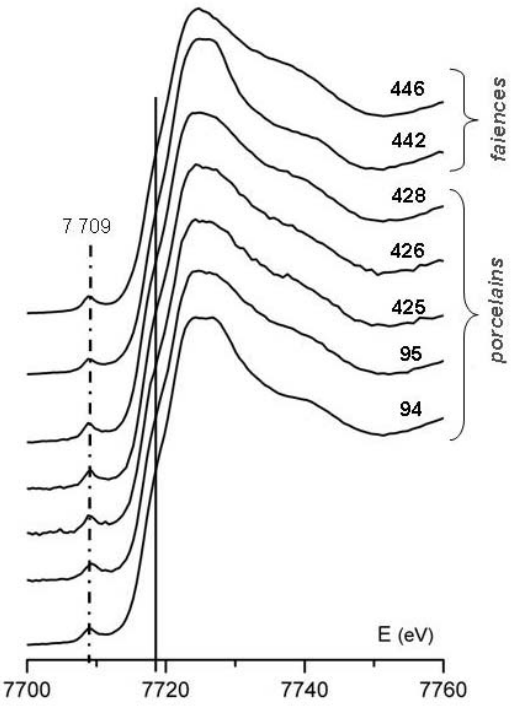

FIGURE 2. Co *K*-edge XANES spectra collected from the blue glaze of studied archaeological fragments.

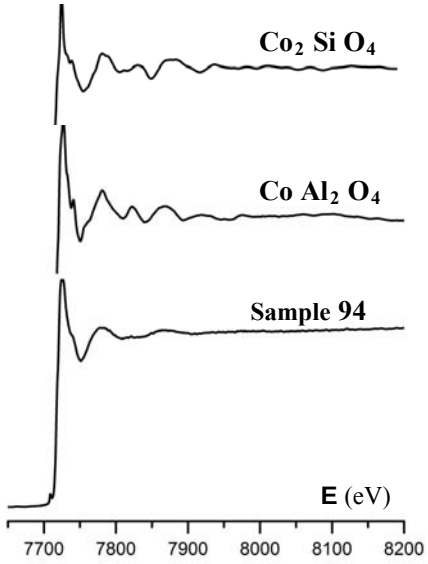

FIGURE 3. Comparison of Co *K*-edge XAFS spectra.

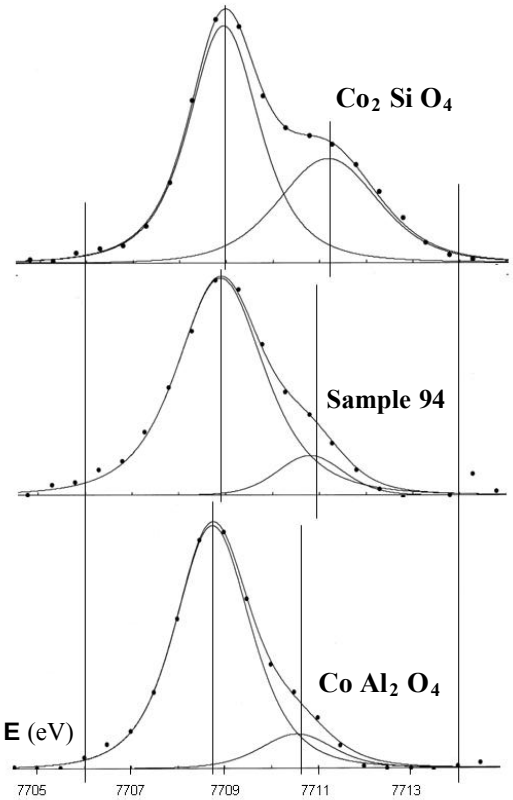

FIGURE 4. Comparison of resolved pre-edge details in Co 1*s* XANES spectra.

Co 1*s* XANES spectra of model oxides present dissimilarities in the near-edge layout as expected for Co^{2+} ions with distinct close oxygen coordination environments - tetrahedral and octahedral, respectively in the spinel $CoAl_2O_4$ and in the silicate Co_2SiO_4.

The pre-edge spectral region was resolved with the Fityk program [12]. When comparing the contributing features obtained for the best-fit in model compounds with similarly resolved details of the XANES spectrum from a porcelain fragment (Figure 4), the prevailing tetrahedral environment around the $3d^7$ transition metal ion Co^{2+} in the Chinese glaze becomes apparent.

The EXAFS spectral region was deconvoluted using the FEFF8 program based on a theoretical multiple scattering approach, along with the supporting IFEFFIT library [13-16]. Calculated pseudo-radial distribution functions (Figure 5) show a similar trend of Co-O distances in the spinel oxide and in the Chinese blue glaze; conversely, dissimilar tendencies are noticed for the silicate in which crystal structure the oxygen octahedra around Co^{2+} ions share edges, thus giving rise to close Co-Co distances.

Using the theoretical amplitudes and the phase parameters calculated with FEFF8, the experimental EXAFS spectra of the porcelains were fitted allowing the coordination number (N), the atomic distances (R) and the Debye-Waller factor (σ^2) to vary freely. Fitting convergence could only be attained with $Co\ Al_2\ O_4$ spectrum as illustrated by Figure 6. Resulting numerical values are 4.4 ± 0.6 Å for the coordination number and ~2.00 Å for the mean Co-O distances, with a Debye-Waller factor of 0.010 ± 0.002 $Å^2$. EXAFS data treatment then validates an average coordination environment close to tetrahedral for most cobalt ions within the glaze.

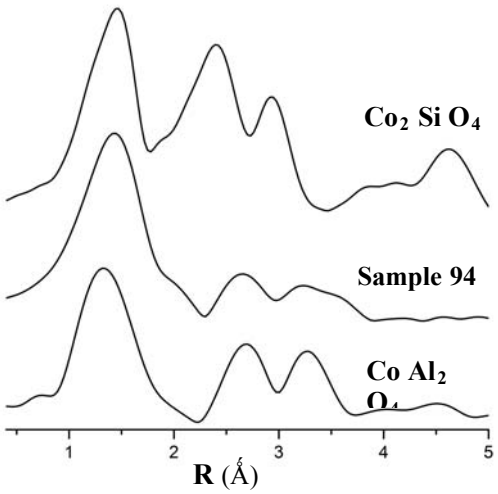

FIGURE 5. Pseudo-radial distribution functions extracted from experimental Co *K*-edge EXAFS spectra.

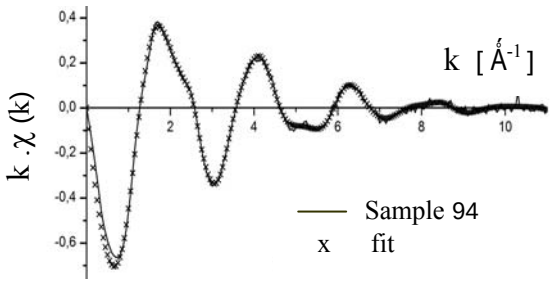

FIGURE 6. Best-fit of experimental data from a porcelain sample to the theoretically calculated spectrum of Co Al_2 O_4.

CONCLUSIONS

Chemical data in general and particularly the absence of arsenic assigned through the present work conform to the dating advanced by Art-Historians through the examination of studied archaeological Chinese porcelain shards (Table 1). Actual results clearly demonstrate that lead – a fuser metal currently used in Portugal to manufacture ceramic glazes along the XVI-XVII century – was not employed to produce contemporary blue Chinese glazes for porcelains, thus providing a distinctive authenticity feature.

Concerning the Chinese porcelain fragments collected at the Monastery of Santa Clara-a-Velha, actual chemical data agree with recent results obtained in a larger study by energy dispersive X-ray micro-fluorescence carried out with a portable apparatus [17].

XAFS results confirm that cobalt plays the dual role of chromophore and network-former in the blue glaze of ancient Chinese porcelains, the tetrahedral Co^{2+} ions being responsible for a blue coloring [18]. Conversely, non-coloring pseudo-octahedral Co^{2+} ions occupy available coordination sites of the tetrahedral silica-rich glassy matrix.

Differences in the pre-edge features of XANES spectra from model oxides are explained by the local symmetry of Co^{2+} ions: regular tetrahedral coordination with site symmetry $\bar{4}$ 3 *m* in Co Al_2 O_4 (spinel-type oxide) and octahedral coordination with two site symmetries ($\bar{1}$ and *m*) in Co_2 Si O_4 (olivine-type crystal structure). In fact, the absorption edge of 1*s* XANES spectra from 3*d* transition metals is due to electronic transitions from the 1*s* core state to the 4 *p* conduction band, while pre-edge details arise from quadrupole transitions to 3*d* empty states; when the inherent inversion symmetry is broken (as in tetra-hedral Co^{2+}, a high spin $3d^7$ ion with filled e_g and t_{2g} orbitals), local 3*d* 4 *p* wave-function mixing allows for dipole transitions to occur [19]. Considering the mean coordination number of Co^{2+} extracted from EXAFS spectra, these comments also account for the XANES results obtained for the studied ancient blue glazes.

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